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Japanese Patent Laid-open No. 49293/1992  
Japanese Patent Laid-open Date: February 18, 1992  
Japanese Patent Application No. 158608/1990  
Japanese Patent Application Date: June 19, 1990  
Int. Cl. C07F 5/06, C08F 4/642  
Applicant: Idemitsu Kosan Co., Ltd.

## SPECIFICATION

### 1. Title of the Invention:

#### ALUMINOXANE SOLUTION AND POLYMERIZATION CATALYST CONTAINING THE SAME

### 2. What is Claimed is:

(1) An aluminoxane solution which comprises an aluminoxane, an aromatic hydrocarbon, and a polar compound.

(2) An aluminoxane solution as defined in Claim 1, wherein the aluminoxane is methylalminoxane.

(3) An aluminoxane solution as defined in Claim 1, wherein the polar compound is a halogenated hydrocarbon.

(4) An aluminoxane solution as defined in Claim 1, wherein the polar compound is a compound which does not contain active hydrogen but has at least one species of oxygen atom, sulfur atom, nitrogen atom, and phosphorus atom.

(5) A polymerization catalyst which comprises an aluminoxane solution as defined in Claim 1 and a transition metal compound.

3. Detailed Description of the Invention:

(Field of industrial application)

The present invention relates to an aluminoxane solution suitable for use as a catalyst component for the production of various polymers, and also relates to a polymerization catalyst composed of said aluminoxane solution and a transition metal compound.

(Prior art and problems to be solved by the invention)

It is known well that the production of olefin polymers and styrene polymers is facilitated by the aid of a catalyst composed of an aluminoxane and a transition metal compound.

An aluminoxane compound is soluble in an aromatic hydrocarbon solvent (such as toluene), but the solution, after long storage, gives rise to viscous gel-like aluminoxane particles, which stick to the container, with a change in aluminoxane concentration.

One way of eliminating this disadvantage by adding alkyl aluminum has been proposed in Japanese Patent Laid-open No. 258686/1989. The addition of alkyl aluminum, however, affects the composition and activity of aluminoxane through alkyl exchange, and hence gives rise to polymers having undesirable properties.

It is an object of the present invention to provide a homogeneous aluminoxane solution which is free of the

above-mentioned problems, stable for a long period of time, and suitable for use as a catalyst component for the production of various polymers.

[Means to solve the problems]

The gist of the present invention resides in an aluminoxane solution which comprises an aluminoxane, an aromatic hydrocarbon, and a polar compound.

The aluminoxane used in the present invention is formed by reaction of an organoaluminum compound with water.

The aluminoxane includes alkylaluminoxane (with an alkyl group having 1-6 carbon atoms), such as methylaluminoxane, ethylaluminoxane, and isobutylaluminoxane, of which the first is most desirable.

The organoaluminum compound as a raw material for aluminoxane is one which is represented by the formula [I]



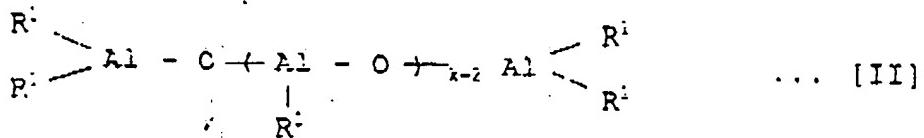
(where R denotes an alkyl group having 1-8 carbon atoms.)

The organoaluminum compound represented by the formula [I] includes trialkylaluminum compounds (such as trimethylaluminum, triethylaluminum, and triisobutylaluminum) and dialkylaluminum monochloride, of which trimethylaluminum is most desirable.

To prepare the aluminoxane, the organoaluminum compound is brought into contact with water, ice, or a water-

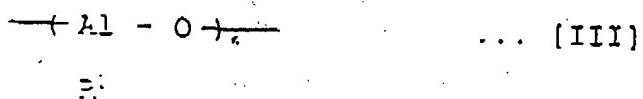
containing compound (such as solvent-saturated water, inorganic substances containing adsorbed water, and metal salts containing water of crystallization, including copper sulfate pentahydrate  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and aluminum sulfate 16 hydrate).

Upon reaction with water, the organoaluminum compound (typical of which is alkylaluminum) yields a linear alkyl-aluminoxane represented by the formula [II] below



(where  $R'$  is defined as above, and  $k$  denotes the degree of polymerization.)

or a cyclic alkylaluminoxane composed of the repeating units represented by the formula [III] below



(where  $P$  is defined as above, and  $k$  denotes the degree of polymerization.) The value of  $k$  is usually 4-52.

When an organoaluminum compound (such as trialkylaluminum) is brought into contact with water, there are obtained, depending on the reaction conditions, unreacted trialkylaluminum, several reaction products, condensation products, and intricately associated compounds, in addition to the above-mentioned linear and cyclic alkylaluminoxanes.

There are no specific restrictions on the reaction between an organoaluminum compound and water. The reaction may be carried out in the usual way. For example:

- (1) an organoaluminum compound is dissolved in an organic solvent, and subsequently the solution is brought into contact with an organic solvent.
- (2) water is dissolved in an organic solvent, and an organoaluminum compound is added to the solution.
- (3) an organoaluminum is reacted with a metal salt containing water of crystallization or an inorganic or organic substance containing adsorbed water.

The reaction may proceed in the absence of solvent; however, the reaction in a solvent is desirable. Preferred examples of the solvent include aliphatic hydrocarbons (such as hexane, heptane, and decane) and aromatic hydrocarbons (such as benzene, toluene, and xylene).

In the present invention, an aromatic hydrocarbon is used as the solvent. Examples of the aromatic hydrocarbon include benzene, toluene, and xylene.

According to the present invention, the aluminoxane solution contains a polar compound. A preferred polar compound is a halogenated hydrocarbon or a compound which does not contain active hydrogen but has at least one species of oxygen atom, sulfur atom, nitrogen atom, and phosphorus atom.

X Examples of the halogenated hydrocarbon include halogenated aliphatic hydrocarbons and halogenated aromatic hydrocarbons, of which chlorobenzene, dichlorobenzene, and trichlorobenzene are desirable.

Examples of the compound which contains no active hydrogens but has oxygen atoms include ethers (such as ethyl ether, isopropyl ether, isoamyl ether, tetrahydrofuran, dioxane, and anisole), ketones (such as methyl ethyl ketone and acetone), and esters (such as dimethyl carbonate and methyl acetate).

Examples of the compound which contains no active hydrogens but has nitrogen atoms include nitriles (such as acetonitrile and benzonitrile) and amines (such as triethylamine).

Examples of the compound which contains no active hydrogens but has sulfur atoms include dimethylsulfoxide.

According to the present invention, the aluminoxane solution comprises an aluminoxane, an aromatic hydrocarbon, and a polar compound, which are exemplified above.

The aluminoxane solution can be prepared by dissolving in the aromatic hydrocarbon and polar compound mixed together the aluminoxane (formed as mentioned above) as such (liquid), in the form of concentrate, or in the form of solid (after drying).

The amount of the aromatic hydrocarbon should be 0.5-

100 g, preferably 1-50 g, per gram of aluminoxane.

The amount of the polar compound should be more than 0.1 mol%, preferably 1-50 mol%, per mol of Al atoms in the aluminoxane.

According to the present invention, the above-mentioned aluminoxane solution is combined with a transition metal compound to give a polymerization catalyst.

There are no restrictions on the transition metal compound; it is usually one which contains a transition metal belonging to the IVB, VB, VIB, VIIIB, and VIII Groups of the Periodic Table.

Examples of the transition metal include titanium, zirconium, hafnium, chromium, manganese, nickel, palladium, and platinum, of which titanium, zirconium, nickel, and palladium are desirable.

Of many transition metal compounds, those which are represented by the formula [IV] are desirable.



In the formula [IV], M denotes a transition metal belonging to the IVB, VB, VIB, VIIIB, and VIII Groups of the Periodic Table; and a, b, c, and d each denotes an integer of 0-7;  $R^1 - R^4$  may be the same or different; and two or more of  $R^1 - R^4$  may combine with one another to form a ring.

In the formula [IV],  $R^1 - R^4$  each denotes any one of

the following. Halogen atom (such as fluorine, chlorine, bromine, and iodine); oxygen atom; C<sub>1-20</sub> alkyl groups (such as methyl group, ethyl group, n-propyl group, iso-propyl group, n-butyl group, t-butyl group, iso-butyl group, octyl group, and 2-ethylhexyl group); C<sub>1-20</sub> alkoxy groups (such as methoxy group, ethoxy group, propoxy group, butoxy group, and phenoxy group); C<sub>6-20</sub> aryl groups (such as phenyl group, tolyl group, xylyl group, and benzyl group); alkylaryl groups or arylalkyl groups; C<sub>1-20</sub> acyloxy groups (such as heptadecyl carbonyloxy group); indenyl group; fluorenyl group; substituted cyclopentadienyl groups (such as cyclopentadienyl group, methylcyclopentadienyl group, ethylcyclopentadienyl group, 1,2-dimethylcyclopentadienyl group, tetramethylcyclopentadienyl group, and pentamethylcyclopentadienyl group); allyl group; substituted allyl group; acetylacetone group; substituted acetylacetone group; substituted silyl groups (such as trimethylsilyl group and (trimethylsilyl)methyl group); carbonyl group; oxygen molecule; nitrogen molecule; ethylene; ethers (such as diethyl ether, tetrahydrofuran THF, and dimethyl ether); esters (such as ethylbenzoate); nitriles (such as acetonitrile and benzonitrile); amines (such as triethylamine, 2,2'-bipyridine, and phenanthroline); phosphines (such as triethylphosphine and triphenylphosphine); iso-cyanides; phosphonic acids; Lewis bases (such as thiocya-

nate); and cyclic unsaturated hydrocarbons (such as benzene, toluene, xylene, cycloheptatriene, cyclooctadiene, cyclooctatriene, and cyclooctatetraene, and derivatives thereof).

It is desirable that the substituent group in R<sup>2</sup> - R<sup>5</sup> be an alkyl group.

There are additional transition metal compounds derived from the formula [IV] above, which are effective as the catalyst component of the present invention. Their examples include the following.

- Zirconium compounds: bis(cyclopentadienyl)zirconium dichloride, bis(cyclopentadienyl)zirconium monohydride monochloride, bis(cyclopentadienyl)dimethylzirconium, bis(cyclopentadienyl)dibenzylzirconium, bis(cyclopentadienyl)zirconium dimethoxide, bis(methylcyclopentadienyl)-zirconium dichloride, bis(pentamethylcyclopentadienyl)-zirconium dichloride, (pentamethylcyclopentadienyl)-zirconium trichloride, (pentamethylcyclopentadienyl)-zirconium trimethoxide, (pentamethylcyclopentadienyl)-tribenzylzirconium, (cyclopentadienyl)zirconium trichloride, (cyclopentadienyl)zirconium tribromide, ethylene bis(indenyl)zirconium dichloride, ethylene bis(tetrahydroindenyl)zirconium dichloride, dimethylsilyl bis(cyclopentadienyl)zirconium dichloride, and dichloro-zirconium bis(acetylacetone).

- Titanium compounds and hafnium compounds: Those zirconium compounds (as mentioned above) in which zirconium is replaced by titanium or hafnium.
- Chromium compounds: tetramethyl chromium, tetra-(t-butyl) chromium, bis(cyclopentadienyl) chromium, hydridetricarbonyl(cyclopentadienyl) chromium, hexacarbonyl(cyclopentadienyl) chromium, bis(benzene) chromium, tricarbonyltris(triphenyl phosphonate) chromium, tris(allyl) chromium, triphenyltris(tetrahydrofuran) chromium, and chromium tris(acetylacetone).
- Manganese compounds: tricarbonyl(cyclopentadienyl) manganese, pentacarbonyl methyl manganese, bis(cyclopentadienyl) manganese, and manganese bis(acetylacetone).
- Nickel compounds: dicarbonyl bis(triphenylphosphine) nickel, dibromobis(triphenylphosphine) nickel, dinitrogen bis(bistricyclohexylphosphine) nickel, chlorohydride bis(tricyclohexylphosphine) nickel, chloro(phenyl) bis(triphenylphosphine) nickel, dimethyl bis(trimethylphosphine) nickel, diethyl(2,2'-bipyridyl) nickel, bis(allyl) nickel, bis(cyclopentadienyl) nickel, bis(methylcyclopentadienyl) nickel, bis(pentamethylcyclopentadienyl) nickel, allyl(cyclopentadienyl) nickel, (cyclopentadienyl)(cyclooctadiene) nickel tetrafluoroborate, bis(cyclooctadiene) nickel, nickel bisacetylacetone, allylnickel chloride, tetrakis(triphenylphosphine) nickel, nickel

chloride, and  $(C_6H_5)Ni\{OC(C_6H_5)CH=P(C_6H_5)_2\}(P(C_6H_5)_3)$ .

• Palladium compounds: dichlorobis(benzonitrile) palladium, carbonyl tris(triphenylphosphine) palladium, dichlorobis(triethylphosphine) palladium, bis(isocyanated t-butyl) palladium, palladium bis(acetylacetone), dichloro(tetraphenylbutadiene) palladium, dichloro(1,5-cyclooctadiene) palladium, allyl(cyclopentadienyl) palladium, bis(allyl) palladium, allyl(1,5-cyclooctadiene) palladium tetrafluoroborate, (acetylacetone) (1,5-cyclooctadiene) palladium tetrafluoroborate, and tetrakis(acetonitrile) palladium ditetrafluoroborate.

According to the present invention, the catalyst contains the above-mentioned aluminoxane solution as one component (organometal compound).

The aluminoxane solution may be used alone or in combination with an organoaluminum compound (represented by the formula [I] above) or any other organometal compound. It may also be used in such a form that it is adsorbed on or carried by an inorganic substance.

The catalyst of the present invention comprises the above-mentioned transition metal compound and aluminoxane solution as the major components. It may also be incorporated with other catalyst components (such as organometal compounds) as required.

The catalyst may vary in composition (the ratio of

the transition metal compound to the aluminoxane solution) depending on the conditions under which it is used. The composition is usually established such that the ratio of aluminum (in the aluminoxane solution) to transition metal (in the transition metal compound) is 1-10<sup>6</sup>, preferably 10-10<sup>4</sup> (in mol).

The catalyst of the present invention exhibits high activity in the production of olefin polymers and styrene polymers (especially those having the syndiotactic structure).

The production of styrene polymers is accomplished by polymerization or copolymerization of styrene and/or styrene derivatives (such as alkylstyrene, alkoxy styrene, halogenated styrene, and vinyl benzoate) in the presence of the catalyst of the present invention.

The production of olefin polymers is accomplished by polymerization or copolymerization of olefins (such as  $\alpha$ -olefins including ethylene, propylene, butene-1, hexene-1, octene-1, 4-methylpentene-1, etc., butadiene, isoprene, norbornadiene, acetylene, and methylacetylene) in the presence of the catalyst of the present invention.

The polymerization may be accomplished by bulk polymerization or solution polymerization (in an aliphatic hydrocarbon solvent such as heptane, hexane, and pentane, an alicyclic hydrocarbon solvent such as cyclohexane, or

an aromatic solvent such as benzene, toluene, and xylene). The polymerization temperature is not specifically limited. It is usually from -30°C to +150°C, preferably from -10°C to +120°C.

It will be possible to control the molecular weight of the desired polymer by properly selecting the amount of the transition metal compound and the polymerization temperature and also by performing the polymerization in the presence of hydrogen.

#### [Examples]

The invention will be described in more detail with reference to the following examples.

##### Example 1

(1) Preparation of an aluminoxane solution: A 1-liter glass container, with the atmosphere therein replaced with argon, was charged with 200 ml of toluene and 35.0 g of copper sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ). To the glass container cooled at 5°C was added dropwise 9.6 g (133 mmol) of trimethyl aluminum. Reaction was carried out at 40°C for 8 hours. After removal of solids, the reaction product was freed of toluene by vacuum distillation at 50°C with stirring. The residue was dried at 110°C until volatile matters disappeared. Thus there was obtained 4.7 g of aluminoxane.

This aluminoxane was dissolved in a mixture of tolu-

ene (20 ml) and *c*-dichlorobenzene (0.9 ml). The alumin-oxane solution was allowed to stand in the atmosphere of ~~dry~~ ~20 wt dry nitrogen for 1 month. It did not give rise to gel-like precipitates during this period.

(2) Polymerization of ethylene: A 1-liter autoclave, with the atmosphere therein replaced by nitrogen, was charged sequentially with 400 ml of toluene, the alumin-oxane solution (prepared in step (1) mentioned above) in an amount equivalent to 1 mmol of aluminum atoms, and 5  $\mu$ mol of biscyclopentadienylzirconium dichloride. With the autoclave heated at 80°C, ethylene was continuously introduced into the autoclave so as to perform polymerization at 8 kg/cm<sup>2</sup> for 1 hour.

After the completion of polymerization, ethanol was added to decompose the catalyst. Upon drying, there was obtained 127 g of polyethylene. The catalyst activity was 278 kg-PE/g-Zr.

(3) Polymerization of styrene: A 1-liter autoclave, with the atmosphere therein replaced by nitrogen, was charged sequentially with 200 ml of styrene, 2 mmol of triisobutyl aluminum, and the aluminoxane solution (prepared in step (1) mentioned above) in an amount equivalent to 2 mmol of aluminum atoms. With the autoclave heated at 70°C, 10  $\mu$ mol of pentamethylcyclopentadienyltitanium trimethoxide was introduced into the autoclave so as to perform poly-

merization for 1 hour.

After the completion of polymerization and upon drying, there was obtained a polymer (85 g). This polymer was found to have a syndiotacticity (in terms of racemic pentad) of 97%, as determined by  $^{13}\text{C}$ -NMR. The catalyst activity was 177.5 kg-SPS/g-Ti.

Comparative Example 1

The same procedure as in Example 1 was repeated to prepare an aluminoxane solution, except that o-dichlorobenzene was not used. It gave rise to gel-like precipitates when it was allowed to stand for 1 month under an atmosphere of dry nitrogen.

Example 2

(1) Preparation of an aluminoxane solution: The same procedure as in Example 1 was repeated to prepare an aluminoxane solution, except that 0.8 ml of dioxane was used in place of o-dichlorobenzene. There was obtained 4.3 g of aluminoxane.

This aluminoxane was dissolved in a mixture of toluene (20 ml) and o-dichlorobenzene (0.9 ml). The aluminoxane solution was allowed to stand in the atmosphere of dry nitrogen for 1 month. It did not give rise to gel-like precipitates during this period.

(2) Polymerization of ethylene: The same procedure as in Example 1 (2) was repeated for ethylene polymerization,

except that the aluminoxane solution was replaced by the one obtained in step (1) mentioned above. The catalyst activity was 246 kg-PE/g-Zr.

(3) Polymerization of styrene: The same procedure as in Example 1 (3) was repeated for styrene polymerization, except that the aluminoxane solution was replaced by the one obtained in step (1) mentioned above. The catalyst activity was 82 kg-SPS/g-Ti.

[Effects of the invention]

The aluminoxane solution of the present invention is homogeneous and has good storage stability, without the possibility of giving rise to gel-like precipitates.

Being free of alkyl aluminum, it remains unchanged in activity and has no adverse effects on the properties of the resulting polymer.

When used as a catalyst component, it improves the catalytic activity for polymerization.

It can be combined with a transition metal compound to give a catalyst which is effective for polymerization of various monomers.